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Structure and Characterization of Sol-gel and Aerogel Materials and Oxidation Products from the Reaction of $(\text{CH}_3\text{O})_4\text{Si}$ and $\text{C}_{16}\text{H}_{33}\text{Si}(\text{OCH}_3)_3$

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ABSTRACT

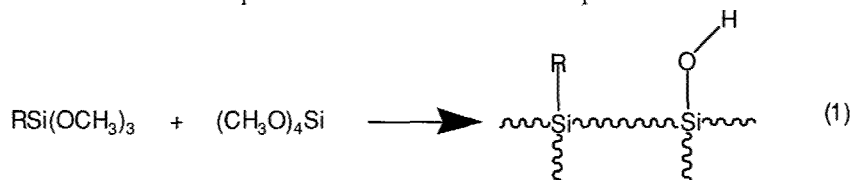
Reactions of $(\text{CH}_3\text{O})_4\text{Si}$ and $\text{C}_{16}\text{H}_{33}\text{Si}(\text{OCH}_3)_3$ at various mole ratios were performed in methanol using base and acid catalysis. Sol-gel materials were formed that have low surface areas ($\sim 10 \text{ m}^2/\text{g}$). Subsequent supercritical drying using CO_2 at 40°C produced materials that are very different than traditional aerogels, with surface areas around the same values as the corresponding sol-gels, as well as no detectable meso-pore features. In some cases, the aerogels even melted upon heating. Spectroscopic characterization, using IR, ^{29}Si and ^{13}C NMR revealed normal Si-O substitution as well as incorporation of the carbon chain into the Si framework.

Heating of the stable forms of the materials in air at different temperatures yielded, depending upon oxidation conditions, several materials with much higher surface areas, typical of aerogels. Pore size distribution measurements revealed meso-pore features with a narrow distribution around 35\AA . Spectroscopic characterization revealed the disappearance of the R-Si substitution and the appearance of an oxidized intermediate.

This paper will describe the chemistry and characterization of these unusual sol-gels, aerogels, and oxidation products, as well as potential applications.

INTRODUCTION

Aerogels are open foam type materials with high surface areas (can be over $1000 \text{ m}^2/\text{g}$), low density (generally 0.1 to 0.3 g/cc), and high porosities (generally 90%) [1]. These materials are extremely interesting and have found many commercial applications, such as insulators, water purification, optics, optic coating, energy storage and chemical sensing [2]. Perhaps the most notable use is in cosmic particle collectors in satellites and space shuttles.



In addition to the unusual base properties of these materials, the chemical properties can also be modified. One method is through incorporation of organic substituted siloxanes into the silica matrix through hydrolysis/condensation reactions, equation 1. This has been shown to be effective for a variety of R groups, yielding new sol-gels or aerogels with modified properties [3]. For example, where $\text{R} = -\text{CH}_2\text{CH}_2\text{CF}_3$, under certain reaction conditions, produces a highly hydrophobic aerogel [4].

In efforts to understand the reaction chemistry of organic/inorganic hybrid materials, several new aerogels with different R groups have been synthesized and characterized. Here we report initial results on utilization of $\text{R} = n\text{-C}_{16}\text{H}_{33}$ in the synthesis of organic/inorganic hybrid aerogels by equation 1. Full results will be published elsewhere.

EXPERIMENTAL

The chemicals were purchased from standard chemical supply companies and used as received. The aerogels were synthesized by methods described previously in detail. The aerogel was formed by mixing 2.0 g (5.8×10^{-3} mol) $\text{C}_{16}\text{H}_{33}\text{Si}(\text{OCH}_3)_3$ and 2.0 g (1.3×10^{-2} mol) $(\text{CH}_3\text{O})_4\text{Si}$ in 7.5 mL of methanol. 200 μL of HBF_4 was added and stirred. Two phases appear initially, but eventually became homogenized. The solution was poured into beakers and were covered with parafilm and left to gel. Gellation took a few seconds. After gellation, the samples were dried either by supercritical CO_2 to form an aerogel or air evaporation to form a xerogel. A typical supercritical extraction solvent exchange took 2 to 4 days.

The supercritical extraction of the aerogels were performed in a SPI Supplies Critical Point Drier. The IR spectra of the samples were taken on a Nicolet Impact 440 spectrometer. The samples were examined either as neat liquid between two NaCl plates or as KBr pellets. The ^{29}Si NMR were taken on a Chemagnetics 300 NMR spectrometer using a Chemagnetics solid state probe. The surface property measurements were taken on a Micromeritic ASAP 2000 upgraded to a ASAP 2010 analyzer. The samples were degassed at 200°C under vacuum before measurements. The surface areas were calculated using the BET model and the meso-pore distributions were calculated using a BJH model. The oxidations were performed in NEY Vulcan 3-1750 temperature controlled furnace. Temperatures were held at $\pm 0.5^\circ\text{C}$.

RESULTS

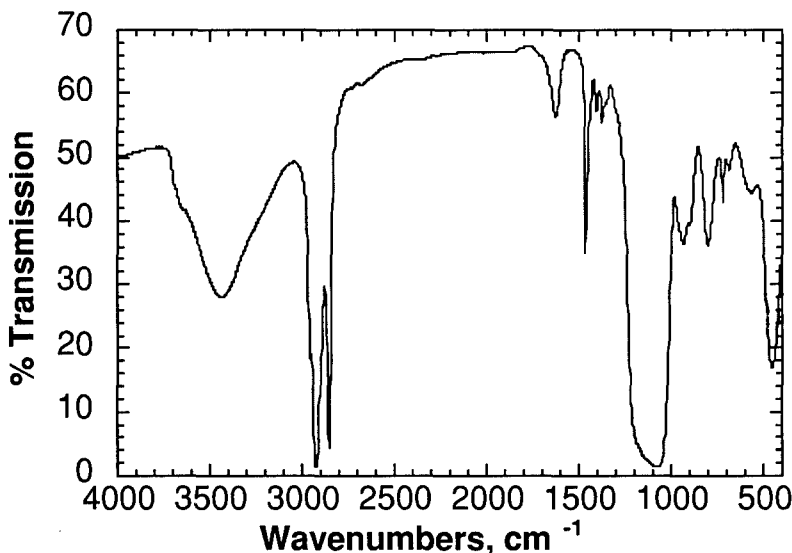


Figure 1. FTIR of the product of $\text{C}_{16}\text{H}_{33}\text{Si}(\text{OCH}_3)_3$ and $(\text{CH}_3\text{O})_4\text{Si}$.

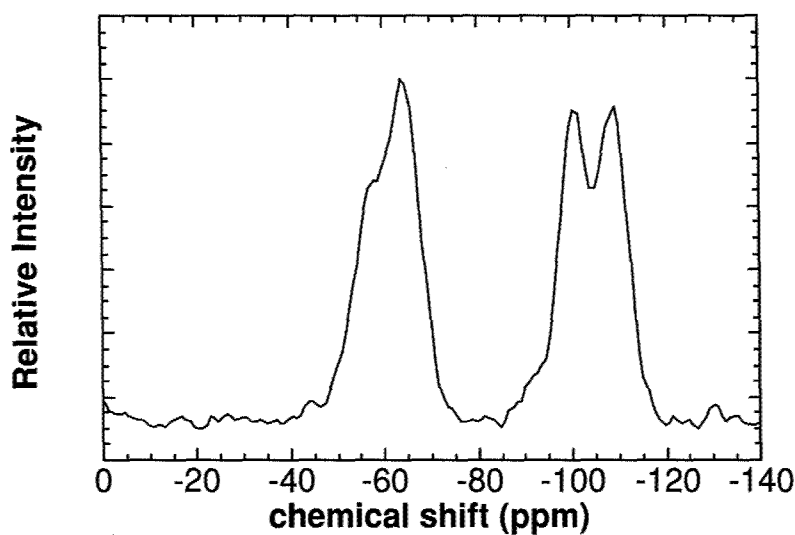


Figure 2. ^{29}Si NMR product of $\text{C}_{16}\text{H}_{33}\text{Si}(\text{OCH}_3)_3$ and $(\text{CH}_3\text{O})_4\text{Si}$.

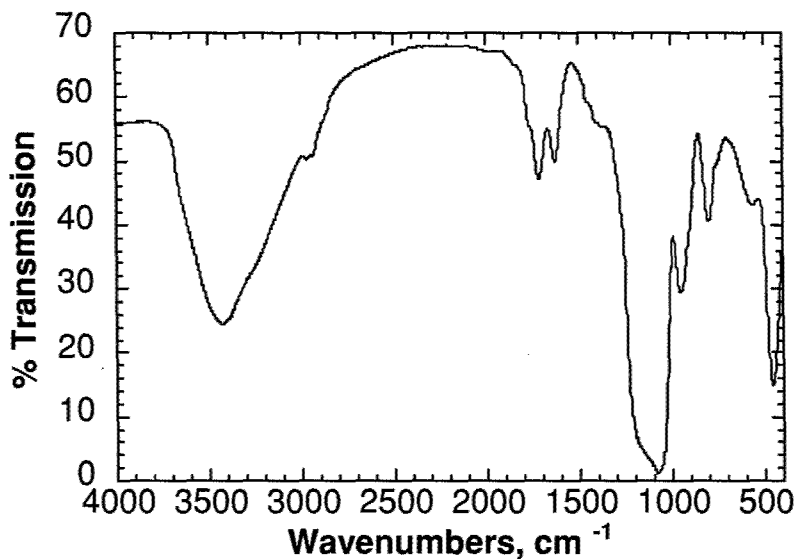


Figure 3. FTIR spectrum of the oxidation of the product of $\text{C}_{16}\text{H}_{33}\text{Si}(\text{OCH}_3)_3$ and $(\text{CH}_3\text{O})_4\text{Si}$ at 300°C for 1h.

Figure 1 shows the IR of the aerogel formed by the reaction of $\text{C}_{16}\text{H}_{33}\text{Si}(\text{OCH}_3)_3$ and $(\text{CH}_3\text{O})_4\text{Si}$ in methanol, shown in equation 1. Clearly evident is a very strong broad feature from

1000 to 1200 cm^{-1} . This is assigned to Si-O-Si of the silica backbone. An overtone feature is also seen at 1640 cm^{-1} . A small medium sharp feature is seen at 960 cm^{-1} assigned to Si-OH. Features indicating the incorporation of the $\text{C}_{16}\text{H}_{33}$ group are seen in the alkyl region of 2800 to 3000 cm^{-1} . A broad feature centered around 3400 cm^{-1} indicating hydrogen bonded materials.

Figure 2 shows the ^{29}Si NMR of the same sample. The features around -110 ppm correspond to the Q_1 through Q_4 substitution distribution for the silica backbone of the aerogel. The features around -60 ppm correspond to Si species with direct C bonds, most likely from the $\text{C}_{16}\text{H}_{33}$ group incorporated.

The surface area of this aerogel was found to be 9 m^2/g , and the meso-pore distribution measurement produced no pore distribution.

Figure 3 shows the IR spectrum of a sample of aerogel oxidized at 300°C for 1 hour. In addition to the features seen in the unoxidized aerogel in Figure 1, features are seen from 1600 to 1850 cm^{-1} . The overtone at 1640 cm^{-1} is now adjacent to a sharper taller feature at 1716 cm^{-1} . Deconvolution of this feature (not shown) shows this envelope contains less intense bands at 1741, 1775, and 1847 cm^{-1} . These bands are assigned to alkyl carboxylic acids, esters, and cyclic anhydrides. In addition to these bands formed by the oxidation, the alkyl features in the 2800 to 3000 cm^{-1} range are decreased in intensity.

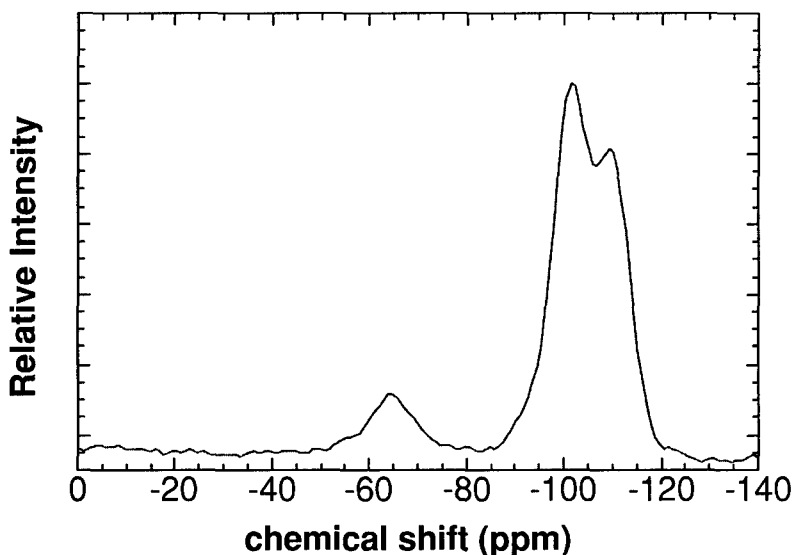


Figure 4. ^{29}Si NMR spectrum of the product of $\text{C}_{16}\text{H}_{33}\text{Si}(\text{OCH}_3)_3$ and $(\text{CH}_3\text{O})_4\text{Si}$ oxidized at 300°C for 4 h

Figure 4 shows the ^{29}Si NMR spectrum of the aerogel oxidized at 300°C for 4 h. The resonances accounting for the Q_1 to Q_4 branching distribution are changed in proportion, but are still visible. The resonance corresponding to the Si-C bond is visible, but is greatly reduced in intensity.

Figure 5 shows the % weight loss of the aerogel at 300°C at different oxidation times. As the oxidation time increases, the amount of weight loss also increases. However, after about 100 min., the % weight appears to reach a upper limit of 45%. There is little difference between the 90 min. data point and the 240 min. data point.

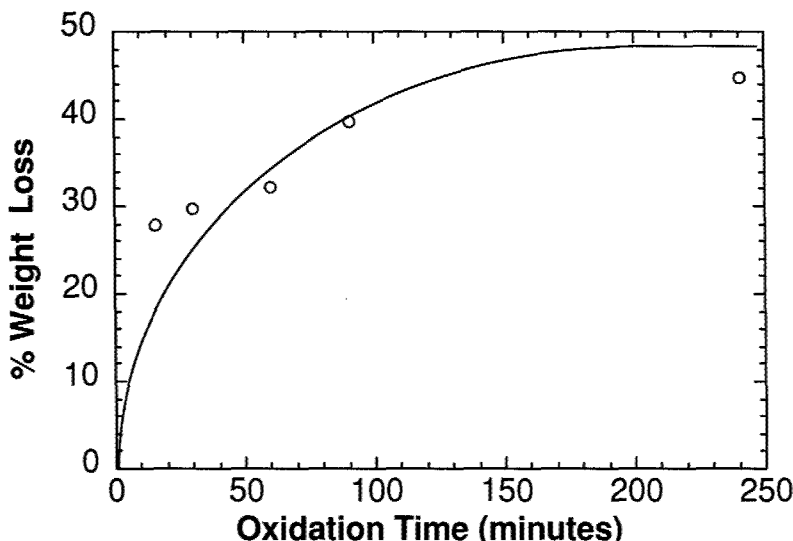


Figure 5. Weight loss of the product of $C_{16}H_{33}Si(OCH_3)_3$ and $(CH_3O)_4Si$ at different oxidation times.

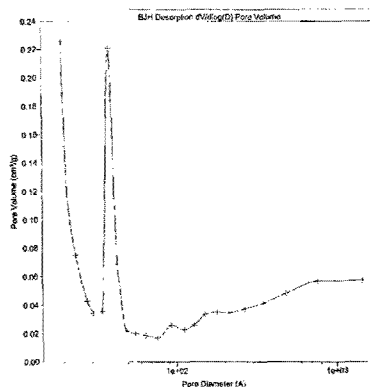


Figure 6. Meso-pore distribution for product of $C_{16}H_{33}Si(OCH_3)_3$ and $(CH_3O)_4Si$ oxidized at 300°C for 1h.

Figure 6 shows the pore size distribution for in the meso-pore range for the sample oxidized at 300°C for 1 h. A sharp pore feature centered at 35Å is visible. Other meso-pore features are seen, but at much lower intensities.

DISCUSSION

The reaction of $C_{16}H_{33}Si(OCH_3)_3$ and $(CH_3O)_4Si$ in methanol utilizing $HB F_4$ catalysis ultimately produced an aerogel that has the R group incorporated, verified by IR and ^{29}Si NMR. Comparison with IR spectra of the starting material and a xerogel produced by the same formulation indicate the sol-gel process incorporates the substituted

siloxane similar to results seen in preparations with other R group substitution [3,4].

Oxidation at 300°C shows various changes in the properties of the aerogel. The IR spectrum indicates carboxylic acids and other carboxylate features that are not present in the un-oxidized aerogel. In addition, the alkyl features appear to be decreasing in intensity relative to the Si-O-Si features. These results suggest the oxidation is logically happening on the C₁₆H₃₃ group, probably forming shorter alkyl carboxylic acids esters and cyclic anhydrides. At 90 min. oxidation, most of the alkyl features in the IR are virtually absent (not shown). This corresponding to the weight loss behavior seen in Figure 5, which appears to reach a maximum around that reaction time. However, some of the carboxylate features are still seen in the 90 min. sample spectrum, although the relative intensities are much reduced compared to other features. The ²⁹Si NMR of the oxidized material supports this behavior. The 60 min. sample (not shown) also shows the presence of the Si bound directly to C, but at a much reduced intensity.

The meso-pore measurements of the oxidized aerogel show the formation of a fairly sharp pore distribution at maximum around 35 Å. All the other oxidized samples exhibited the same type of pore distribution at the same place, except with different intensities. This must be a result of the oxidation because the non-oxidized aerogel has no meso-pore features. This could possibly due to the oxidation of the C₁₆H₃₃ group leaving a void space, or the structural rearrangement of the aerogel itself. However, the same behavior occurs when the aerogel is oxidized at 200°C suggesting aerogel structural rearrangement is unlikely.

Because of the very low surface area and non-existent meso-pore distribution of the non-oxidized aerogel, it can be argued that this material is not an aerogel. A xerogel produced by the same formulation but left to air dry has a similar surface area, and no meso-pore distribution. The oxidation of the aerogel does produce a sharp meso-pore distribution. This suggests that in the formation of the sol-gel, the R group is so large that it fills the void spaces in the silica matrix that normally lead to standard aerogel meso-pores. The C₁₆H₃₃ group is long and flexible and probably folds onto itself into a ball, filling these voids. Alternatively, the group is so large that the sol-gel forms around it, forcing a structure that has no meso-pore size voids.

ACKNOWLEDGMENT

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